→ Periodic table and Periodic properties:→

- To study the chemistry of elements and their compounds, elements are classified in different ways:-

1. Dobereiner's triads:-

- Dobereiner arranged certain elements with similar properties in a group in such a way that the atomic weight of the middle element was arithmetic mean of other two. This is called law of Triads.

Element	Atomic weight
Li	7
Na	23
K	39

2. In 1862, A.E.B. De Chancoortois arranged elements in order to increasing atomic weight and made a cylindral table of elements but did not attract more attention.

3. Newlond's law of Octaves:→

- Newland arranged elements in order to increasing atomic masses and every eight element has properties similar to the first.

4. Lother Meyer's curve :→

- Lother Meyer plotted the physical properties against atomic weight and obtained a periodically repeated pattern.

5. Mendeleev's Periodic Table :→

- Mendeleev arranged elements in horizontal rows and vertical coloums of a table in order of their increasing atomic weights in such a way that the elements with similar properties occupied the same vertical coloum or group.
- Mendeleev was published a law, called periodic law and according to this law, "The properties of the elements are periodic function of their atomic weights."

6. Modern periodic law and the present form of the periodic table :→

- In the beginning of 20th century, various theories were developed to know about subatomic particles of the an atom and these theories showed that the atomic number is a more fundamental property of an element than its atomic mass.
- Mendeleev's periodic law was, therefore modified. This is known as modern periodic law and according to this law, " The physical and chemical properties of the elements are periodic functions of their atomic numbers."
- A modern version is called long form of the periodic table of the elements.
- The horizontal rows are called periods (7 periods) and vertical colums are called groups (18 groups).
- All elements are classified into four blocks on the basis of the atomic orbitals that are filled with the electrons.

1. The 's' block elements :→

- Group 1 (IA) and 2 (IIA)
- Group 1 → alkali metals → E.C. → [Noble gas]ns^1
- Group 2 → alkaline earth metals → E.C. → [Noble gas]ns^2
- The 's' block elements are also called light metals

2. The 'p' block elements :→

- Group 13 (III A) to 18 (VIII A)
- Nonmetals and posttransition metals.
- p-block elements together with s-block elements are called main group elements or representative elements.
- E.C. → [Noble gas]ns^2np^1 to [Noble gas]ns^2np^6
- Group 15 elements are called Pnictogens → greek word → peígein → meaning → to choke
- Group 16 elements are called Chalcogens → greek word → chalcos → meaning → Ore forming
- Group 17 elements are called Halogens → hal (salt) + gen (producing) → Salt producing
- Group 18 elements are called Noble gases

3. The 'd' block elements :→

- Transition elements.
- E.C. → [Noble gas]$(n-1)d^{1-10}\,n^{0-2}$
- Group → 3 (III B), 4 (IV B), 5 (V B), 6 (VI B), 7 (VII B), 8, 9, 10 (VIII B), 11 (IB), 12 (IIB)

4. The 'f' block elements:→

- Lanthenide elements → Ce(58) to Lu(71)
- Actinide elements → Th(90) to Lr(103)
- E.C. → [Noble gas] $(n-2)f^{1-14}(n-1)d^{0-10}ns^2$
- Called Inner transition metals.
- Actinides elements are radioative.
- The elements after Uranium are called Transuranium elements.

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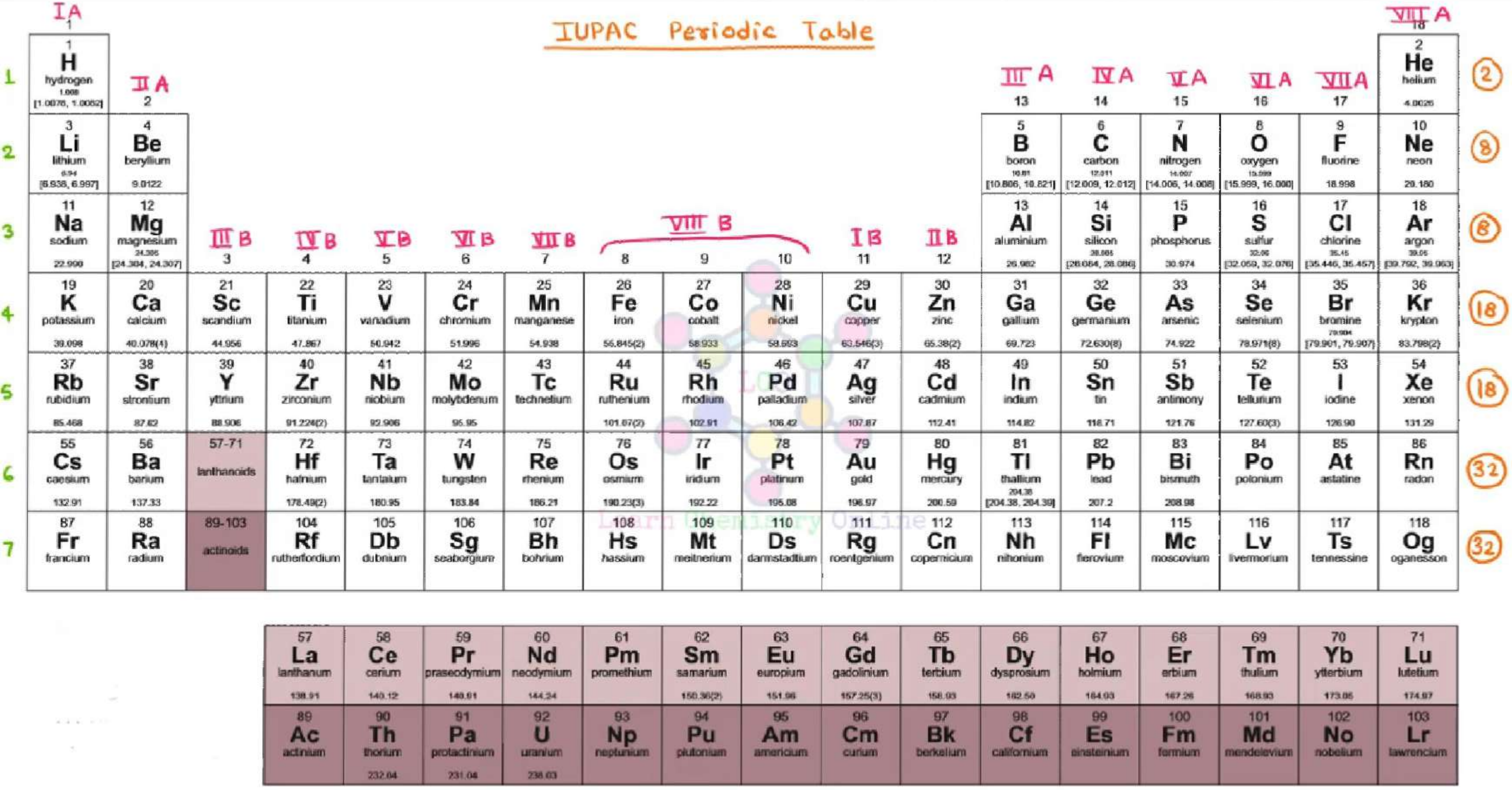
IUPAC Periodic Table



	IA 1	IIA 2	IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	VIII B 8	 9	 10	IB 11	IIB 12	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	VIIIA 18	
1	1 **H** hydrogen 1.008 [1.0078, 1.0082]																	2 **He** helium 4.0026	②
2	3 **Li** lithium 6.94 [6.938, 6.997]	4 **Be** beryllium 9.0122											5 **B** boron 10.81 [10.806, 10.821]	6 **C** carbon 12.011 [12.009, 12.012]	7 **N** nitrogen 14.007 [14.006, 14.008]	8 **O** oxygen 15.999 [15.999, 16.000]	9 **F** fluorine 18.998	10 **Ne** neon 20.180	⑧
3	11 **Na** sodium 22.990	12 **Mg** magnesium 24.305 [24.304, 24.307]											13 **Al** aluminium 26.982	14 **Si** silicon 28.085 [28.084, 28.086]	15 **P** phosphorus 30.974	16 **S** sulfur 32.06 [32.059, 32.076]	17 **Cl** chlorine 35.45 [35.446, 35.457]	18 **Ar** argon 39.95 [39.792, 39.963]	⑧
4	19 **K** potassium 39.098	20 **Ca** calcium 40.078(4)	21 **Sc** scandium 44.956	22 **Ti** titanium 47.867	23 **V** vanadium 50.942	24 **Cr** chromium 51.996	25 **Mn** manganese 54.938	26 **Fe** iron 55.845(2)	27 **Co** cobalt 58.933	28 **Ni** nickel 58.693	29 **Cu** copper 63.546(3)	30 **Zn** zinc 65.38(2)	31 **Ga** gallium 69.723	32 **Ge** germanium 72.630(8)	33 **As** arsenic 74.922	34 **Se** selenium 78.971(8)	35 **Br** bromine 79.904 [79.901, 79.907]	36 **Kr** krypton 83.798(2)	⑱
5	37 **Rb** rubidium 85.468	38 **Sr** strontium 87.62	39 **Y** yttrium 88.906	40 **Zr** zirconium 91.224(2)	41 **Nb** niobium 92.906	42 **Mo** molybdenum 95.95	43 **Tc** technetium	44 **Ru** ruthenium 101.07(2)	45 **Rh** rhodium 102.91	46 **Pd** palladium 106.42	47 **Ag** silver 107.87	48 **Cd** cadmium 112.41	49 **In** indium 114.82	50 **Sn** tin 118.71	51 **Sb** antimony 121.76	52 **Te** tellurium 127.60(3)	53 **I** iodine 126.90	54 **Xe** xenon 131.29	⑱
6	55 **Cs** caesium 132.91	56 **Ba** barium 137.33	57-71 lanthanoids	72 **Hf** hafnium 178.49(2)	73 **Ta** tantalum 180.95	74 **W** tungsten 183.84	75 **Re** rhenium 186.21	76 **Os** osmium 190.23(3)	77 **Ir** iridium 192.22	78 **Pt** platinum 195.08	79 **Au** gold 196.97	80 **Hg** mercury 200.59	81 **Tl** thallium 204.38 [204.38, 204.39]	82 **Pb** lead 207.2	83 **Bi** bismuth 208.98	84 **Po** polonium	85 **At** astatine	86 **Rn** radon	(32)
7	87 **Fr** francium	88 **Ra** radium	89-103 actinoids	104 **Rf** rutherfordium	105 **Db** dubnium	106 **Sg** seaborgium	107 **Bh** bohrium	108 **Hs** hassium	109 **Mt** meitnerium	110 **Ds** darmstadtium	111 **Rg** roentgenium	112 **Cn** copernicium	113 **Nh** nihonium	114 **Fl** flerovium	115 **Mc** moscovium	116 **Lv** livermorium	117 **Ts** tennessine	118 **Og** oganesson	(32)

57 **La** lanthanum 138.91	58 **Ce** cerium 140.12	59 **Pr** praseodymium 140.91	60 **Nd** neodymium 144.24	61 **Pm** promethium	62 **Sm** samarium 150.36(2)	63 **Eu** europium 151.96	64 **Gd** gadolinium 157.25(3)	65 **Tb** terbium 158.93	66 **Dy** dysprosium 162.50	67 **Ho** holmium 164.93	68 **Er** erbium 167.26	69 **Tm** thulium 168.93	70 **Yb** ytterbium 173.05	71 **Lu** lutetium 174.97
89 **Ac** actinium	90 **Th** thorium 232.04	91 **Pa** protactinium 231.04	92 **U** uranium 238.03	93 **Np** neptunium	94 **Pu** plutonium	95 **Am** americium	96 **Cm** curium	97 **Bk** berkelium	98 **Cf** californium	99 **Es** einsteinium	100 **Fm** fermium	101 **Md** mendelevium	102 **No** nobelium	103 **Lr** lawrencium

→ Periodicity of Properties :→

- The term periodicity of properties indicates that the elements with similar properties reappear at certain regular intervals of atomic number in the periodic table.

Example:→

Periodic number	group 1 (1A)	
1	$_{1}H$	2
2	$_{3}Li$	8
3	$_{11}Na$	8
4	$_{19}K$	18
5	$_{37}Rb$	18
6	$_{55}Cs$	32
7	$_{87}Fr$	

- In other words we can say that the atomic number intervals at which the elements with similar properties reappear are 2, 8, 8, 18, 18, 32.
- The repetition of the elements with similar properties is the order of increasing atomic number as in the periodic table is called periodicity of properties and numbers 2, 8, 8, 18, 18, 32 are called magic numbers.
- The elements of same group show similar properties due to similar valence shell electronic configurations.
- The word periodic means with the rise of atomic number of the elements in the same period or group, there is a gradual variation (i.e. increase or decrease) in a particular property of the element.

— Some of such type of properties are -

① Atomic and Ionic radii

② Ionisation energy.

③ Electron affinity

④ Electronegativity

→ Atomic radius or Atomic radii :→

- The term atomic radius is generally used for distance between the nucleus and outermost shell of the atomic particle.
- Since it is impossible to isolate an individual atom, it is not possible to measure the atomic radius.
- The atomic radius, therefore, measured from the internuclear distance (distance between to nuclei of two bonded atoms in a gaseous molecule.
- The internuclear distances are generally determined by x-Ray diffraction, electron diffraction, NMR spectroscopy techniques etc.

→ Classification of Atomic radii :→

- Atomic radii are sub-divided into three classes:-

(1) Covalent radii (in non-metals and in covalent molecules)
(2) Metallic or crystal radii (in metals)
(3) Van der Waals or collision radii

(1) Covalent radii :→

- It is defined as half of the distance between the nuclei of the two same atoms bonded together by a single covalent bond.

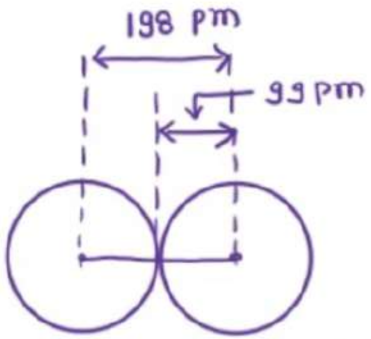


fig:- Internuclear distance and covalent radii (Cl_2 molecule)

- In case of homonuclear di atomic molecule A_2, the bond length or internuclear distance is equal to sum of single-bond covalent radii of both the atoms.

$d_{A-A} = r_A + r_A$ here d_{A-A} = bond length or internuclear distance

or $d_{A-A} = 2r_A$ r_A = covalent radii of single-bonded atom.

or $\boxed{r_A = \frac{d_{A-A}}{2}}$

e.g. Cl_2 molecule :- $d_{A-A} = 198$ pm , $r_A = \frac{198}{2}$, $r_A = 99$ pm

- In case of heteronuclear diatomic molecule AB

ⓐ If electronegativity of A and B is same.

$\boxed{d_{A-B} = r_A + r_B}$ here d_{A-B} = bond lenth or internuclear distance of molecule AB

r_A & r_B = covalent radii of single-bonded atom A & B

ⓑ If electronegativity of A and B is different.

- According to Schomaker and Stevenson -

$\boxed{d_{A-B} = r_A + r_B - 0.09(\chi_A - \chi_B)}$ here :- χ_A & χ_B electronegativities of atom A and B.

- According to Pauling-

$\boxed{d_{A-B} = r_A + r_B - C(\chi_A - \chi_B)}$ here :- C = Schomaker and stevenson coefficient.

- Type of covalent radii :-

(i) Single-bond covalent raddi — involve single bond

(ii) Double-bond covalent raddi — involve double bond
(iii) Triple-bond covalent raddi — involve triple bond
} are called multiple-bond covalent radii

② Metallic or crystal radii :→

- This is used for metal atoms which are assumed to be closely packed sphere in the metallic crystal.
- It is defined as half of the distance between the nuclei of two adjacent metal atom in the metallic close packed crystal lattice in which metal shows a coordination number of 12.

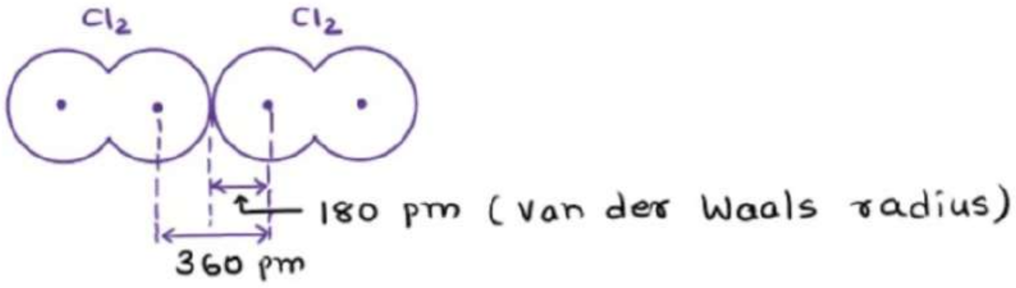
Example :- Internuclear distance between two adjacent Na-atoms in a crystal of Sodium metal is 380 pm.

The metallic radii of Na atom is $\frac{380}{2} = 190$ pm.

③ Van der Waals or Collision radii :→

- The individual non-metallic molecules are held together by Van der Waals forces.
- Van der Waals is half of the distance between the nuclei of two non-bonded neighbouring atoms of two adjacent molecules.

Example :- The distance b/w Cl-atoms of two different molecule is 360 pm. Thus Van der Waals radii of Cl-atom is $\frac{360}{2} = 180$ pm.



- Comparision of covalent, Metallic and Van der Waals radius:-

Covalent radii < Metallic radii < Van der Waals radii

- Periodic variations of Atomic radii :->
- Atomic radii is a periodic function of the atomic number i.e. it changes with the change of atomic number in the periodic table as shown below-

ⓐ In a period :->

- Atomic radii decreases from left to right across in a period in the periodic table when we consider only normal elements. e.g. In case of 2nd period, the atomic radius decreases as we move from Li to F.
- Explaination :->
- The number of shell in the elemements of given period remains the same but value of effective nuclear charge increases from left to right. The increased effective nuclear charge pull the e- cloud of element nearer to nucleus and thus size of atoms goes on decreasing from left to right.

ⓑ In a group :→

- On moving down a group of regular elements atomic radii increases with increasing atomic number. e.g. In group 2 (IIA), atomic radii increases from Be to Ba.
- Explaination :→
- On proceeding downwards in a group the electrons are added to higher energy level which are farther from nucleus. This effect decreases electrostatic attraction b/w nucleus and valence-shell e^- and this decreases the atomic radii.
- With increasing atomic number, effective nuclear charge is also increases but decrease in electrostatic attraction is predominant. As a result, atomic radii decrease in group on moving downwards.
- Factors affecting the magnitude of Atomic radii :→

① Effective nuclear charge :→

$$\text{Effective nuclear charge} \propto \frac{1}{\text{Atomic radii}}$$

② Number of shell or principal quantum no. :→

$$\text{Number of shell or principal quantum no.} \propto \text{Atomic radii}$$

→ Ionic radius or Ionic radii :→

- The term Ionic radius is generally used for distance between the nucleus and outermost shell of the ionic particle.
- Since it is impossible to isolate an individual ion , it is not possible to measure the ionic radius.
- The ionic radius, therefore , measured from the interionic distance (distance between to nuclei of two bonded ions in a crystal or a solid.
- The interionic distances are generally determined by x-Ray diffraction , electron diffraction, NMR spectroscopy techniques etc.
- Ionic radius may be defined as the distance between the nucleus of an ion and the point upto which the nucleus has influence on its e^- cloud.
- The Ionic radii have an additive character. i.e. the interionic distance b/w two ions is equall to the sum of the radii of ions.

$$\boxed{d_{(C^+-A^+)} = r(C^+) + r(A^-)}$$

here C^+ = Cation , A^- = Anion

Example :- Calculate ionic radius of Cl^- ion in NaCl if Na^+-Cl^- = 276 pm and Na^+ = 95pm

$$d_{(Na^+-Cl^-)} = r(Na^+) + r(Cl^-)$$

$$276 = 95 + r(Cl^-)$$

$$r(Cl^-) = 276 - 95 = 181 \text{ pm}$$

- Factors affecting the magnitude of Ionic radii :→

① Effective nuclear charge:→

$$\text{Effective nuclear charge} \propto \frac{1}{\text{Ionic radii}}$$

② Number of shell or principal quantum no:→

$$\text{Number of shell or principal quantum no.} \propto \text{Ionic radii}$$

- Periodic variations of Ionic radii :→

- Ionic radii is a periodic function of the atomic number i.e. it changes with the change of atomic number in the periodic table as shown below—

ⓐ In a period:→

- Ionic radii decreases from left to right across in a period in the periodic table when we consider only normal ions. e.g. In case of 2nd period, the ionic radius decreases as we move from Li to F.

- Explaination :→

- The number of shell in the elemements of given period remains the same but value of effective nuclear charge increases from left to right. The increased effective nuclear charge pull the e⁻ cloud of element nearer to nucleus and thus size of ions goes on decreasing from left to right.

ⓑ In a group :→

- On moving down a group of regular elements ionic radii increases with increasing atomic number. e.g. In group 2 (IIA), ionic radii increases from Be^{+2} to Ba^{+2}

- Explaination :→

- On proceeding downwards in a group the electrons are added to higher energy level which are farther from nucleus. This effect decreases electrostatic attraction b/w nucleus and valence-shell e⁻ and this decreases the ionic radii.
- With increasing atomic number, effective nuclear charge is also increases but decrease in electrostatic attraction is predominant. As a result, ionic radii decrease in group on moving downwards.
- A cation is smaller in size than its parent neutral atom :-
- A cation is formed by the removal of electrons. After removing electrons the effective nuclear charge is increases. This makes the cation smaller in size than its parent neutral atom.
- An anion is bigger in size than its parent neutral atom :-
- An anion is formed by the addition of electrons. After addition of electrons the effective nuclear charge is decreases. This makes the anion bigger in size than its parent neutral atom.

- Radii of isoelectronic series:-

- The radii of isoelectronic series decreases with increase in atomic number (z).

Isoelectronic species →	O^{-2}	F^-	Ne	Na^+	Mg^{+2}
Ionic radii (pm) →	140	136	112	95	65

- Determination of Ionic radii :→

1. Lande's Method:-

- If anion touch one another then anion-anion distance is given by

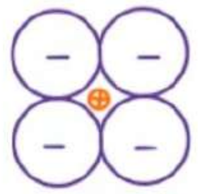


fig:- Anions touch one another

$$d_{(A^- - A^-)} = r(A^-) + r(A^-)$$

$$\text{or } d_{(A^- - A^-)} = 2r(A^-)$$

$$\text{or } r(A^-) = \frac{d_{(A^- - A^-)}}{2}$$

Example:- In case of LiI = $d_{(I^- - I^-)} = 432$ pm

$$r(I^-) = \frac{432}{2} = 216 \text{ pm}$$

- If cation touches the anion then cation-anion distance is given by

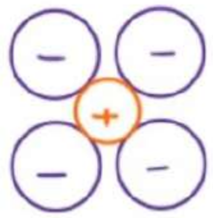


fig:- Cation touches anion

$$d_{(c^+ - A^-)} = r(c^+) + r(A^-)$$

Example In case of KI = $d_{(K^+ - I^-)} = 349$ pm , $I^- = 216$ pm

$349 = r(c^+) - 216$, $r(c^+) = 349 - 216$, $r(c^+) = 133$ pm

2. Pauling's method:→

- According to Pauling, If the cations and anions are in contact with each other then interionic or internuclear distance is given by

$$\boxed{d_{(C^+-A^-)} = r(C^+) + r(A^-)} \text{ ——— } ①$$

- According to Pauling, the relationship b/w radii of ions and effective nuclear charge is given by

$$\boxed{\frac{r(C^+)}{r(A^-)} = \frac{[Z_{eff}]_{A^-}}{[Z_{eff}]_{C^+}}} \text{ ——— } ②$$

- If values of $d_{(C^+-A^-)}$, $[Z_{eff}]_{A^+}$ and $[Z_{eff}]_{C^+}$ are given then we can calculate value of $r(C^+)$ and $r(A^-)$ with the help of eq. ① and ②.

→ Ionisation energy :→

- The amount of energy required to remove the most loosely bound electron (i.e. the outermost electron) from an isolated gaseous atom of an element in its lowest energy state (ground state) to produce a cation is known as ionisation energy of that element.

$$\underset{\text{Isolated gaseous atom}}{M(g)} + \underset{\text{Ionisation energy}}{\text{Energy supplied}} \longrightarrow \underset{\text{Cation}}{M^+(g)} + e^-$$

- The process by which the element loses an electron to convert itself into a cation is called its ionisation. This process is an endothermic process, since energy is supplied to effect it.
- Ionisation energy is also called ionisation potential, since it represents the amount of potential or voltage required to remove an electron.
- Ionisation energy is measured in electron volts per atom (eV/atom), kilo calories per mole (Kcal/mole) or kilo joules per mole (KJ/mole). These quantities are related as –

1 eV/atom = 96.47 KJ/mole = 23.06 KCal/mole
1 Kcal/mole = 4.185 KJ/mole

- The values of ionisation potential are shown by +ve sign. positive sign represents absorption of energy by the atom.

→ Successive ionisation potential:→

- The electrons are removed in stages one by one from an atom. The amount of energy required to remove the first electrom from a gaseous atom is called first ionisation potential.
- The energy required to remove second electron from the cation is called second ionisation potential. similarly we have third, fourth--- ionisation potentials. Thus

$$M(g) + I_1 \longrightarrow M^{+}(g) + e^-$$

$$M^{+}(g) + I_2 \longrightarrow M^{+2}(g) + e^-$$

$$M^{+2}(g) + I_3 \longrightarrow M^{+3}(g) + e^-$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

- The order of successive ionisation potential is

$$I_1 < I_2 < I_3 < I_4 < ---$$

The successive increase in their values is due to fact that it is relatively more difficult to remove an electron from a cation having higher positive charge than a cation having lower positive charge or from a neutral atom.

→ Factors affecting the magnitude of Ionisation potential :→

1. Effective nuclear charge :→

- With increase of the magnitude of effective nuclear charge, the magnitude of ionisation potential also increases.

$$\boxed{\text{Effective nuclear charge} \propto \text{Ionisation potential}}$$

2. Atomic size :→

- With increasing atomic size, magnitude of ionisation potential is decreases

$$\boxed{\text{Atomic size} \propto \frac{1}{\text{Ionisation potential}}}$$

3. Principal quantum number (n) :-

- With the increase of the principal quantum number (n) of the orbital from which the electron is to be removed, the magnitude of ionisation potential decreases.

$$\boxed{\text{Principal quantum number} \propto \frac{1}{\text{Ionisation potential}}}$$

4. Shielding effect :→

- With increasing shielding effect, magnitude of ionisation potential is decreases.

$$\text{Shielding effect} \propto \frac{1}{\text{Ionisation potential}}$$

5. Penetration effect :→

- For a given value of n the degree of penetration effect will decrease in the order

$$\boxed{s > p > d > f}$$

The s-e⁻ will approach the nucleus more closely than p-e⁻, a p-e⁻ is more closely than d and d more closely than f. Thus it is difficult to remove s-electron. hence s have highest value of ionisation potential.

6. Half-filled and completely filled orbitals :→

- According to Hund's rule, atoms having half-filled or completely-filled orbitals are comparatively more stable and hence more energy is needed to remove an electron from such atoms. This means that ionisation potential of such atom is relatively higher than expected normally from its position in the periodic table.

- Periodic variation in ionisation potential :→

① In a period :-

- From left to right in a period, the ionisation potential of the elements increases due to the successive increase in the nuclear charge (i.e. atomic number) and decrease in atomic size. However there are certain elements which show irregular trends.

- Large increase in the value of ionisation potential from H to He
- H = 1320.0 KJ/mole He = 2372.3 KJ/mole
- In case of He, both the electrons are present in 1s orbital, the first electron is unable to shield the second. This increases the ionisation potential of He atom.
- Large decrease in the value of ionisation potential from He to Li

  He = $1s^2$ → 2372.3 KJ/mole   Li = $1s^2 2s^1$ → 520.3 KJ/mole
- It is easy to remove electron from 2s (n=2) as compare to 1s (n=1).
- In case of Li, electron to be removed from 2s orbital is effectively shielded by the 1s electrons while in He, electron to be removed from 1s orbital is not effectively shielded by another 1s-electron.
- Be has higher ionisiation potential than B.

  Be = $1s^2 2s^2$ B = $1s^2 2s^2 2p^1$
- In case of Be, it is more difficult to remove an electron from completely filled 2s-orbital while in case of B, it easier to remove an electron from incompletely filled 2p-orbital. Since removal of electron from 2s required higher energy hence Be has higher ionisation potential than B.
- N has higher ionisation potential than O.

  N = $1s^2 2s^2 2p^3$ O = $1s^2 2s^2 2p^4$

- In case of N, it is more difficult to remove an electron from the half-filled 2p orbital while in case of O, it is easier to remove an electron from the incompletely filled 2p-orbital. Thus the ionisation potential of N is higher than O.
- Large decrease in the value of ionisation potential from Ne to Na

  Ne = $1s^2 2s^2 2p^6$ → 2080.7 KJ/mole , Na = $1s^2 2s^2 2p^6 3s^1$ → 495.8 KJ/mole
- It is easy to remove electron from 3s (n=3) as compare to 2p (n=2).
- In case of Na, electron to be removed from 3s orbital is effectively shielded by the 8 e− (2nd shell) while in He, electron to be removed from 2p orbital is not effectively shielded by another five electrons.
- Mg has higher ionisation potential than Al

  Mg = $1s^2 2s^2 2p^6 3s^2$ Al = $1s^2 2s^2 2p^6 3s^2 3p^1$
- In case of Mg, it is more difficult to remove an electron from completely filled 3s-orbital while in case of Al, it easier to remove an electron from incompletely filled 3p-orbital. Since removal of electron from 2s required higher energy hence Mg has higher ionisation potential than Al.
- P has higher ionisation potential than S

  P = $1s^2 2s^2 2p^6 3s^2 3p^3$ S = $1s^2 2s^2 2p^6 3s^2 3p^4$
- In case of P, it is more difficult to remove an electron from the half-filled 3p orbital while in case of S, it is easier to remove an electron from the incompletely filled 3p-orbital. Thus the ionisation potential of P is higher than S.

- Second ionisation potential of N is less than second ionisation potential of O :-

  $N^+ = 1s^2 2s^2 2p^2$ $O^+ = 1s^2 2s^2 2p^3$

- In case of N, it is easy to remove an e- from incompletely 2p orbital while in case of O, it is difficult to remove an e- from half-filled 2p orbital.

② In a group:→

- On proceeding from top to bottom in a group of representotive elements, the ionisation potential values of the elements go on decreasing. This is due to increase in atomic size from top to bottom in a group.
- However there are some exception.
- Al and Ga have approx. same value of ionisation potential:-
- It is due to low shielding of d-orbital e^- present in Ga.
- Tl has high ionisation potential than In :-
- It is due to low shielding of f- orbital e^- present in Tl

→ Applications of the concept of Ionisation potential:→

① To determine the metallic and non-metallic character from Left to right in periodic table.

→ Loft side of periodic table → low ionisation potential → easily to loose e^- → metals

→ Right side of periodic table → high ionisation potential → does not easily lousee e^- → non-metals

② Relative reactivity of elements:-

High ionisation potential → less reactive (inert gases)

Low ionisation potential → more reactive (Group 1 & Group 2 elements)

③ Reducing power of an element :-

$$\text{Ionisation potential} \propto \frac{1}{\text{Reducing agent}}$$

④ Basic character of an element :-

$$\text{Ionisation potential} \propto \frac{1}{\text{Basic character}}$$

⑥ Determination of valence shell electron in an atom :-

- With the help of ionisation potential values, no. of valence shell electrons in an atom can be calculated.

example :- For Li , First IP = 5.4 eV and second IP = 75.6 eV.

These values show that 1 e⁻ can be remove easily than the other. Thus Li has only one e⁻ in their valence shell.

→ Determination of ionisation potential :-

- The following methods are used for determination of ionisation potential -

1. Spectroscopic methods.
2. Photoionization method
3. Electron impact method
4. Quantum mechanical method.

→ Electron affinity (EA or $\Delta_{eg}H$) :→

- The amount of energy released when an electron is added to an isolated gaseous atom in its lowest energy state (i.e. ground state) to produce an anion is called electron affinity.

$$\underset{\text{Neutral gaseous atom}}{A(g)} + e^- \longrightarrow \underset{\text{Anion}}{A^-(g)} + \underset{\text{Electron affinity}}{\text{Energy released } (-EA)}$$

- Electron affinity is also called electron affinity energy.
- The above process by which the neutral gaseous atom adds an electron is an exothermic process, since energy is released in it and is represented with a –ve sign.
- Electron affinity is measured in electron volts, kilocalories or kilojules.
- The energy released on the addition of first electron is called first electron affinity and addition of second electron is called second electron affinity.

In the process of adding an electron to an anion, $A^-(g)$ againt electrostatic repulsion between the electron being added and the negative charge on $A^-(g)$ ion, energy instead of being released is supplied to $A^-(g)$ to form $A^{-2}(g)$

$$A(g) + e^- \longrightarrow A^-(g) + \text{Energy released } (-EA_1) \text{ (Exothermic)}$$

$$A^-(g) + e^- + \text{Energy supplied } (+EA_1) \longrightarrow A^{-2}(g) \text{ (Endothermic)}$$

→ Factors affecting the magnitude of electron affinity :→

1. Effective nuclear charge :→

- with the increase of effective nuclear charge, the magnitude of electron affinity also increases.

$$\boxed{\text{Effective nuclear charge} \propto \text{Electron affinity}}$$

2. Atomic Size :→

- Smaller atoms have higher electron affinities.

$$\boxed{\text{Atomic size} \propto \frac{1}{\text{Electron affinity}}}$$

3. Shielding effect :→

- with increasing shielding effect, the magnitude of electron affinity decreases.

$$\boxed{\text{Shielding effect} \propto \frac{1}{\text{Electron affinity}}}$$

4. Completely filled, Half filled and Incompletely filled orbitals.

- Completely and half filled orbitals have low electron affinities.
- Icompletely filled orbitals have high electron affinities.

→ Periodic variation in the electron affinity :→

① In a period :→

- Electron affinity values generally increase on moving from left to right in a period in the periodic table.
- However there are some exceptions.
- Be and Mg have zero electron affinities

$Be = 1s^2 2s^2$ $Mg = 1s^2 2s^2 2p^6 3s^2$

- Since Be and Mg have completely filled s-orbitals, the additional electron will be entering the 2p in case of Be and 3p in case of Mg which are of higher energy than 2s and 3s orbitals.
- Inert gases have zero electron affinities
- In case of inert gases, ns and np orbitals are completely filled, the incoming electron must go into an electron shell have larger value of n. Thus inert gases have zero electron affinity.
- N and P have low electron affinities

$N = 1s^2 2s^2 2p^3$ $P = 1s^2 2s^2 2p^6 3s^2 3p^3$

- This is because of the presence of half filled orbitals which are relatively more stable and hence to which it is difficult to add an additional electron.

② In a group :→

- In moving down to a group electron affinity values generally decreases. This is due to increase in the atomic radius of the elements.
- However there are some exceptions.
- Electron affinities of second period elements is less than elements of third period.
- This unexpected behaviour is explained by saying that the much smaller size of the second period elements give a very much higher value of charge densities for the respective negative ion. This charge density opposes incoming e^-.

  e.g. Electron affinity of F is less than Cl
- Applications of Electron affinity :→

① To determine the metallic and non-metallic character of element from left to right in period.

Left side of periodic table → Low electron affinity → does not accept e^- easily → metals

Right side of periodic table → high electron affinity → easily accepts e^- → non-metals

② Oxidising power of an element :→

$$\boxed{\text{Electron affinity} \propto \text{oxidising agent}}$$

③ Acidic nature of an element :→

$$\boxed{\text{Electron affinity} \propto \text{Acidic nature}}$$

④ Reactivity of an electronegative element :→

Electron affinity $\propto$ Reactivity of an electronegative element

→ Determination of Electron affinity :→

- Electron affinity can be measured using Born-Haber cycle.

→ Electronegativity (EN) :→

- When two different atoms in a molecule are bonded together by a covalent bond, the electron pair forming the covalent bond is not shared equally by the both the atoms. Rather, the electron pair lies nearer to one atom than the other.
- The relative tendency (or ability or power) of a bonded atom in a molecule to attract the shared electron pair towards itself is termed as its electronegativity.
- Electron affinity represents the tendency of an isolated gaseous atom to attract the electrons while electronegativity represents the tendency of a bonded atom of a molecule to attract the shared electron pair.

→ Factors affecting the magnitude of electronegativity :→

1. Atomic size :→

- The smaller atom have greater electronegativity value.

$$\boxed{\text{Atomic size} \propto \frac{1}{\text{Electronegativity}}}$$

2. Number of inner shells :- (No. of shell between nucleus and outermost shell)

- The atom with greater number of inner shells has less value of electronegativity :-

$$\boxed{\text{No. of inner shells} \propto \frac{1}{\text{Electronegativity}}}$$

3. Charge on cation :→

- The element in higher positive oxidation state has more value of electronegativity.

Positive oxidation state ∝ Electronegativity

- Electronegativity order

$$M^{+2} > M^{+} > M$$

4. Number and nature of atoms to which the atom is bonded :-

- The electronegativity of an atom is depend on the number and nature of atoms bonded to it

e.g. Electronegativity of P is different in PCl_3 and PF_5 molecules.

5. Ionisation energy and Electron affinity :-

- The elements which have higher value of ionisation energy and electron affinity also have higher value of electronegativity.

e.g. - halogen have higher values of ionisation energy, electron affinity & electronegativity.

- Alkali metals have lower values of ionisation energy, electron affinity & electronegativity.

6. Type of hybridisation :→

- The magnitude of electronegativity increases as the s-character of hybrid orbital increases.

Hybridisation	sp^3	sp^2	sp
s-character	25%	33.3%	50%

Electronegativity $\xrightarrow[\text{Increasing}]{}$

→ Periodic variations in the electronegativity :→

① In a period :→

- Electronegativity increases on moving in a period of the periodic table from left to right. This is due to decrease in the size of atom from left to right in a period.

② In a group :→

- On moving down through a group of the periodic table, the electronegativity decreases. This is due to increase in the size of atom from top to bottom in a group.
- The most electronegative element, F present at top right hand corner of the periodic table while most electropositive element, Cs present at the bottom left hand corner.

→ Scales of Electronegativity : Measurement of Electronegativity :→

1. Pauling scale :→

- Given by Pauling in 1932.
- Consider a molecule AB, in which the electronegativity difference is given by the following equation

$$\boxed{\chi_A - \chi_B = K\left[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}\right]^{1/2}} \quad -①$$

here K = constant = 0.208

χ_A & χ_B = Electronegativities of atom A and B

E_{A-B} = Bond energy of bond A–B

E_{A-A} = Bond energy of bond A–A

E_{B-B} = Bond energy of bond B–B

or

$$\boxed{\chi_A - \chi_B = 0.208\left[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}\right]^{1/2}} \quad -②$$

- Equation ② can be used to calculate χ value of an atom if χ value of another atom is given. Pauling measured electronegativity in eV :

2. Mulliken Scale :→

- Given by mulliken in 1934.
- Mulliken suggested that electronegativity is related to ionisation potential and electron affinility and the basis of above statement, he derived following formula –

$$\boxed{\chi_A = \frac{(IP)_A + (EA)_A}{2}} \quad \text{— ①}$$

here χ_A = Electronegativity of atom A

IP = Ionisation potential of atom A

EA = Electron affinity of atom A

- Eq. 1 is used when IP and EA are given in eV. If these values are given in kilocalories then following eq. can be used –

$$\boxed{\chi_A = \frac{(IP)_A + (EA)_A}{2 \times 62.5}} \quad \text{— ②}$$

- Mulliken's values of electronegativity are about 2.8 times large as Pauling's values. hence to make Mulliken's values equal to Pauling's values, right hand side of eq. ① is divided by 2.8.

$$\boxed{\chi_A = \frac{(IP)_A + (EA)_A}{2 \times 2.8} = \frac{(IP)_A + (EA)_A}{5.6}} \quad \text{— ③}$$

- Component $1/5.6$ is called scale adjacement factor. This factor is used when IP and EA are given in eV.

3. Sanderson's scale :-

- Given by Sanderson in 1955.
- This scale is based on stability ratio (SR).

$$\boxed{SR = \frac{ED}{ED_h}} \quad -①$$

here ED = Average electron density

ED_h = Hypothetical electron density, which the atom would have, if it is an inert gas atom.

- According to sanderson electronegativity of atom, A, is given by

$$\boxed{(\chi_A)_{Sanderson} = SR = \frac{ED}{ED_h}} \quad -②$$

Eq. ② is called Sanderson's equation.

- According to Sanderson, ED can be calculated by the following equation-

$$\boxed{ED = \frac{Z}{\frac{4}{3}\pi r^3} = \frac{3Z}{4\pi r^3} = \frac{Z}{4.19r^3}}$$

here Z = Nuclear charge/Atomic No.

r = Non-covalent radius of the atom

- Relationship between Pauling scale and Sanderson scale is given by-

$$\boxed{\chi_{Pauling} = 0.21\,\chi_{Sanderson} + 0.77}$$

4. Allred and Rochow's Scale :-

- Given by Allred and Rochow in 1958.
- This scale is based on covalent radius.
- According to this scale, electronegativity of an atom is the force of attraction between the nucleus of one atom and an electron of an adjacent atom bonded to it and separated from the nucleus by the covalent radius.
- The electronegativity can be calculated by following equation -

$$\chi_A = \frac{Z_{eff}\, e^2}{r^2} \quad -①$$

here Z_{eff} = Effective nuclear charge
e = charge of electron
r = distance b/w nucleus and electron (Å)

- If we compare this scale with Pauling scale, then corrected Allred and Rochow's equation is given by -

$$(\chi_A)_{AR} = 0.359 \frac{Z_{eff}}{r^2} + 0.744 \quad -②$$

or

$$(\chi_A)_{AR} = 0.359 \frac{Z-\sigma}{r^2} + 0.744 \quad -③$$

here $Z_{eff} = Z - \sigma$ (slater's Rule)
σ = Screening constant

→ Applications of Electronegativity concept :→

1. Nature of bond :-

- Consider a molecule, AB, in which χ_A and χ_B are electronegativities of atom A and B.

if $\chi_A = \chi_B$, then A–B bond is non-polar covalent bond or simply covalent bond

if $\chi_A > \chi_B$, then A–B bond is polar covalent bond $(A^{-\delta} - B^{+\delta})$

if $\chi_A >> \chi_B$, then A–B bond is ionic or polar bond $(A^- - B^+)$

2. Percentage ionic character in a polar covalent bond :-

- consider a molecule, AB, in which χ_A and χ_B are electronegativities of atom A and B.

if $\chi_A - \chi_B = 1.9$, A–B bond, 50% Ionic + 50% Covalent

if $\chi_A - \chi_B < 1.9$, A–B bond, Ionic character less than 50% and covalent character more than 50%.

if $\chi_A - \chi_B > 1.9$, A–B bond, Ionic character more than 50% and covalent character less than 50%.

3. Acidic and basic character of XOH molecule in aqueous solution:-

XOH (X = metal or non-metal)

if $\chi_O - \chi_X < \chi_O - \chi_H$ then O–H bond will more polar than X–O bond hence ionisation of XOH molecule will takes place according to following equation-

$$X{-}O \vdots H + H_2O \longrightarrow XO^- + H_3O^+$$

here XOH gives H+ ion therefore behaves like an acid.

if $\chi_O - \chi_X > \chi_O - \chi_H$ then X–O bond will more polar than O–H bond hence ionisation of XOH molecule will takes place according to following equation-

$$X \vdots O-H + H_2O \longrightarrow [X-OH_2]^+ + OH^-$$

here XOH gives OH^- ion therefore behaves like a base.

4. Diagonal relationship :→

- Two elements having almost same electronegativities will show diagonal relationship.

5. Formula and naming of binary compounds :-

- Highly electronegative elememt is written later while writing formula and name of binary compound.

e.g. ICl – Iodine chloride OF_2 – Oxygen difluoride
Cl_2O – Chlorine monoxide

Exceptions :- NH_3 – Ammonia

6. Calculation of Bond length :→

- Bond lenth can be calculated by using Schomaker and Stevenson equation-

$$\boxed{d(A-B) = r(A) + r(B) - 0.09(\chi_A - \chi_B)}$$

where d(A–B) = Bond length of molecule AB
$r(A)$ = Radius of atom A
$r(B)$ = Radius of atom B
χ_A and χ_B = Electronegativities of atom A and B.

7. Metallic and Non-metallic character of an element :-

Low electronegativity → Metallic character.

High electronegativity → Non-metallic character.

8. Colour of Salt :-

Ionic character less than 20% → Compound is coloured

Ionic character more than 20% → Compound is colourless

e.g.

	AgCl	AgBr	AgI	Ag_2S
Ionic character	80%	24%	15%	4%
Colour	White	Pale yellow	yellow	Black